

## Structural Studies on the Rare Earth Carboxylates

### 8. The Crystal and Molecular Structure of Monoclinic Tris(hydroxyacetato)europium(III), $\text{Eu}(\text{HOCH}_2\text{COO})_3$

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The crystal and molecular structure of monoclinic  $\text{Eu}(\text{HOCH}_2\text{COO})_3$  has been determined from three-dimensional X-ray intensity data. The space group is  $P2_1$  and the lattice parameters are  $a = 8.614(3)$  Å,  $b = 8.074(2)$  Å,  $c = 8.478(2)$  Å, and  $\beta = 117.91(1)^\circ$ . The structure is based on 1560 reflexions, the intensities of which were estimated visually from Weissenberg films. It has been refined to a final  $R$ -value of 0.087. The structure is a three-dimensional network formed by ligand chains aligned along  $b$ . The ligands within the chains are held together by hydrogen bonding and the various chains are cross-linked by coordination of the oxygen atoms to europium. The metal ion is nine-coordinated with a coordination polyhedron of the tri-capped trigonal prism type. All ligands are bonded as chelates with the hydroxy oxygen in the equatorial, and one of the carboxylate oxygens at a corner position of the prism. The three remaining corners are occupied by carboxylate oxygens from ligands which are chelated to neighbouring europium atoms.

Powell and Farrell<sup>1</sup> studied the solubility of anhydrous lanthanoid tris-glycolates and found that the temperature dependence of the solubility was different for the La, Ce, Pr, and Nd compounds as compared to the corresponding Sm, Eu, and Gd phases. The authors remarked that "... these anomalies can be explained by differences in crystal structure, but no work has been done to confirm such a hypothesis". This remark gave the idea for a search for anhydrous rare earth tris-glycolates with crystal structures different from the orthorhombic phase described in a previous communication.<sup>2</sup> The existence of a monoclinic  $\text{M}(\text{HOCH}_2\text{COO})_3$  phase has now been established for the elements praseodymium-terbium and the crystal and molecular structure of the corresponding europium(III) compound, abbreviated Euglyc, will be described in this communication.

## EXPERIMENTAL

*Preparation of rare earth triglycolates.* Rare earth triglycolates were obtained by mixing solutions of the various rare earth chlorides with a solution of sodium glycolate in the molar ratio 1:3. Monoclinic phases of the composition  $MC_3H_7O_9$  were obtained for the elements praseodymium and neodymium if the crystals were formed at a temperature below 5°C. The samarium and europium compounds were obtained by crystallization at room-temperature while the gadolinium and terbium compounds could be prepared only at temperatures above 70°C. All attempts to prepare the monoclinic phase for lanthanum and cerium(III) failed. A more detailed account of the phase relationships among the rare earth glycolates will be given in a following communication.<sup>3</sup>

The crystals obtained were prismatic *b*. Analyses of the europium compound gave the following result

	Eu	C	H	
Found	40.3	19.4	2.8	(%)
Calc.	40.3	19.1	2.4	(%)

where the experimental values are compared with those calculated for  $EuC_3H_7O_9$ . The analyses of the other isostructural compounds were in all respects comparable with the result cited above and showed that all solids had the composition  $MC_3H_7O_9$ .

*X-Ray diffraction work.* Powder photographs of the various compounds were obtained by using a Guinier-Hägg focusing camera with  $CuK\alpha$  radiation. The method used has been described previously.<sup>3</sup>

Integrated equi-inclination Weissenberg photographs were taken with Zr-filtered Mo-radiation using the multi-film technique (three films separated by tin foils). Two single crystals were used in recording the layers  $h0l-h9l$  and  $hk0$ , respectively. Their dimensions were  $0.08 \times 0.21 \times 0.08$  mm<sup>3</sup> and  $0.02 \times 0.05 \times 0.02$  mm<sup>3</sup>. All intensities were estimated visually by using a calibrated scale. Of the 1560 independent reflexions measured, 980 were within the copper reflexion sphere, corresponding to 80 % of the possible number.

The linear absorption coefficient for the sample was 61 cm<sup>-1</sup> and all intensities were corrected for absorption. The transmission factors, evaluated by numerical integration, were in the range 0.58–0.71.

*Computations.* All computing work was done on the CDC 3600 computer at Uppsala, Sweden. The programmes used were CELSIUS, DATAP2, DRF, LALS, DISTAN, PLANE, and ORTEP.<sup>4</sup>

## UNIT CELL AND SPACE GROUP

Accurate values of the cell parameters were obtained by least-squares refinement of powder data. Preliminary values of these parameters, used for indexing the powder photographs, were obtained from oscillation and Weissenberg data of Euglyc. The experimental values of  $hkl$  and  $\sin^2\theta$  are given in Table 1 and the refined cell constants in Table 2.

The crystals are monoclinic and contain two formula units per unit cell. The only condition limiting possible reflexions is  $0k0$  absent for  $k \neq 2n$ , *i.e.* the space groups  $P2_1$  and  $P2_1/m$  are indicated.  $P2_1$  is the most probable one as judged from the distribution of vectors in the Patterson maps, and the fact that the unit cell contains two formula units.

## DETERMINATION AND REFINEMENT OF THE STRUCTURE

The position of the europium atom was deduced from the Harker section  $P(u, \frac{1}{2}, w)$ . The oxygen and carbon atoms were located in the electron density maps, calculated from a difference synthesis based upon the known europium

Table 1. Powder data for the monoclinic rare earth triglycolates  $MC_2H_3O_6$ . The observed values of  $\sin^2\theta \times 10^4$  are denoted obs, while the corresponding quantities calculated from the refined lattice parameters given in Table 2 are denoted calc.

h k l	Pr		Nd		Sm		Eu		Gd		Tb		Intensity
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	
0 0 1	101.2	105.3	102.2	106.1	104.1	105.5	104.6	105.8	106.4	106.3	106.9	106.9	s
1 0 -1	109.9	110.2	111.0	110.6	113.2	110.8	112.8	111.0	114.2	111.6	114.4	112.0	s
0 1 1	197.2	196.4	192.7	197.3	196.3	196.5	195.7	197.0	197.5	198.2	199.1	198.9	vs
1 1 -1	200.4	201.3	201.4	201.9	204.0	201.8	204.5	202.2	204.9	203.5	204.0	204.0	vs
2 0 -1	320.1	319.1	322.2	319.6	318.4	320.3	319.5	321.1	322.5	323.8	324.4	325.1	m
1 0 -2	-	328.9	-	331.2	329.7	330.4	330.7	331.1	333.9	332.2	337.6	333.7	m-
0 2 0	362.7	364.5	361.6	365.1	365.3	364.0	364.8	364.9	366.4	367.8	367.7	368.0	s
0 0 2	-	421.3	-	424.3	420.2	422.1	421.2	423.2	429.1	425.0	428.6	427.7	mt
2 0 -2	440.8	440.7	441.2	442.4	447.8	443.0	445.5	444.0	-	446.3	-	447.8	m
0 2 1	467.3	469.8	467.7	471.2	474.4	474.8	472.8	470.7	-	474.0	-	475.0	m-
1 2 -1	-	474.6	477.3	475.7	-	-	-	475.9	-	479.4	-	480.0	-
2 2 -1	681.4	683.6	686.5	684.7	685.4	684.4	684.9	686.0	689.6	691.6	691.9	693.1	m
1 2 -2	-	693.4	-	696.3	693.5	694.4	698.2	696.0	701.4	700.0	705.2	701.8	s
1 0 2	728.5	717.7	-	721.8	719.1	718.3	720.9	720.2	725.3	724.7	729.4	729.7	s
0 2 2	789.2	785.7	-	789.4	783.1	786.2	785.7	788.0	790.7	792.8	794.2	795.7	n
3 1 -1	832.8	823.3	828.2	824.2	824.5	825.3	828.1	827.5	835.3	835.0	837.2	838.3	s
3 0 0	914.2	918.4	916.4	919.8	925.2	919.7	918.9	922.3	930.4	931.1	935.9	935.0	s
0 3 1	927.2	925.4	926.1	927.6	-	924.6	926.1	926.8	-	933.7	-	935.0	e
0 0 3	944.7	947.9	-	954.6	-	949.8	948.7	952.1	955.6	956.3	961.3	962.2	e
3 1 0	-	1010	1014	1011	1016	1011	1019	1014	1027	1023	1033	1028	m-
0 3 2	1243	1243	1248	1246	1239	1241	1243	1244	1247	1252	1254	1256	s
4 0 -2	1276	1276	1271	1278	1274	1281	1277	1284	1298	1295	1304	1300	mt
3 2 0	-	1283	1286	1285	1289	1284	1292	1287	-	1299	-	1304	s
2 0 -4	1318	1316	1327	1325	1322	1322	1328	1324	-	1329	1331	1335	n
4 0 -3	1410	1414	1418	1418	1420	1421	1422	1423	1435	1434	1441	1439	s
3 0 -4	1436	1437	1446	1445	1445	1445	1448	-	1454	-	1459	-	m-
3 3 -1	-	1552	1553	1554	1552	1553	1554	1557	1569	1571	1575	1574	n
1 3 -3	-	1578	1587	1585	-	1580	1580	1584	1596	1593	1598	1597	s
2 3 -3	1599	1593	-	1599	1599	1596	1605	1599	-	1609	1605	1613	mt
4 0 0	-	1633	1633	1635	1636	1635	1642	1640	1651	1655	1661	1665	s
0 0 4	1680	1685	1693	1697	1683	1689	1693	1693	1702	1700	1716	1711	w
4 2 -1	1712	1714	1716	1716	1716	1717	1725	1721	1740	1737	1747	1744	w
1 4 1	1759	1760	1759	1766	1759	1761	1763	1765	1782	1779	1781	1782	w
2 4 -1	-	1777	-	1780	1775	1776	1779	1781	1790	1795	1795	1797	m-
0 4 2	-	1879	1892	1895	1877	1878	1883	1883	1893	1896	1897	1900	m-
2 3 2	-	2038	2053	2045	2034	2033	2045	2045	2059	2059	2074	2068	vwv
3 3 1	-	2135	2143	2140	-	2135	2138	2141	-	2159	2166	2168	vwv
1 0 -5	2252	2249	2267	2266	-	2256	2260	2261	2267	2269	2276	2282	vwv

Table 2. Unit cell parameters and volumes of the monoclinic tris(hydroxyacetato)lanthanoid(III) compounds.

Metal	a/Å	b/Å	c/Å	β/deg	V/Å³
Pr	8.633(13)	8.083(6)	8.502(4)	117.98(4)	523.9(9)
Nd	8.634(6)	8.070(3)	8.480(2)	118.03(2)	521.5(4)
Sm	8.618(5)	8.082(3)	8.480(2)	117.89(1)	522.0(4)
Eu	8.614(3)	8.074(2)	8.478(2)	117.91(1)	521.1(3)
Gd	8.576(6)	8.040(2)	8.462(2)	117.90(2)	515.6(4)
Tb	8.559(5)	8.037(2)	8.443(1)	117.99(1)	512.8(4)

position. These maps contain a spurious mirror plane, but the atoms belonging to one enantiomorphous set were easily located using the interatomic distances in the previously described orthorhombic  $Gd(HOCH_2COO)_3$  structure.<sup>2</sup>

The interlayer scale factors, the preliminary atomic coordinates and the estimated temperature factors for all atoms were then improved by full-matrix, least-squares refinement. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  with weighting according to Cruickshank.<sup>5</sup> The reflexions where  $1.25 < |F_o|/|F_c| < 0.80$  were given zero weight in the refinement. The atomic scattering factors for the neutral atoms were taken from *International Tables*<sup>6</sup> (oxygen and carbon) and from Cromer *et al.*<sup>7</sup> (europium).

After six cycles of refinement, the conventional discrepancy index  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$  had converged to 0.098 while the weighted  $R$ -factor  $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  was equal to 0.108. Three more cycles, now with anisotropic thermal parameters for europium, gave  $R = 0.087$ , and  $wR = 0.095$ . The difference between the two sets of weighted  $R$  values is significant and the following structure description will be based on the parameters obtained

Table 3. Coordinates and thermal parameters for the various atoms in Euglyc, with the space group  $P2_1$  (No. 4). The anisotropic thermal parameters for europium have been calculated by the expression:  $\exp[-(h^2\beta_{11} + hk\beta_{12} + \dots)]$ .

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/\text{\AA}^2$
O(1)	COO <sup>-</sup>	4583(26)	-1382(28)	4726(27)	2.3(3)
O(2)	COO <sup>-</sup>	7137(24)	-2581(25)	6871(26)	1.9(3)
O(3)	-OH	6534(21)	1013(23)	4172(22)	1.6(2)
C(1)	COO <sup>-</sup>	6365(34)	-1461(33)	5704(34)	2.1(4)
C(2)	COH	7603(30)	-142(62)	5482(31)	2.7(4)
O(4)	COO <sup>-</sup>	482(22)	1194(25)	-368(21)	1.6(2)
O(5)	COO <sup>-</sup>	-2266(27)	2189(30)	-962(28)	2.4(3)
O(6)	-OH	643(25)	-619(28)	2411(26)	2.3(3)
C(3)	COO <sup>-</sup>	-826(28)	1350(30)	16(28)	1.6(3)
C(4)	COH	-842(36)	522(38)	1564(37)	2.5(4)
O(7)	COO <sup>-</sup>	4498(21)	1950(22)	435(21)	1.5(2)
O(8)	COO <sup>-</sup>	4110(29)	3301(31)	-2045(30)	2.6(3)
O(9)	-OH	2761(24)	-772(26)	-1339(24)	1.9(3)
C(5)	COO <sup>-</sup>	3879(26)	2005(28)	-1298(27)	1.5(3)
C(6)	COH	2831(37)	564(42)	-2422(38)	2.7(4)
Eu		3413(1)	0(0)	1832(1)	-

$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
49(1)	27(10)	33(1)	-60(4)	26(1)	-11(4)

Table 4. Analysis of the weighting scheme. The averages of  $w(|F_o| - |F_c|)^2 = w\Delta^2$  are normalized and the weighting scheme used is equal to  $w = 1/(60.0 + |F_o| + 0.008|F_o|^2 + 0.0015|F_o|^3)$ .

$ F_o $ interval	Number of reflexions	$w\Delta^2$	$\sin\theta$ interval	Number of reflexions	$w\Delta^2$
0.0 - 23.6	136	0.99	0.00 - 0.28	232	0.95
23.6 - 25.9	135	1.11	0.28 - 0.35	230	0.96
25.9 - 27.8	144	1.08	0.35 - 0.40	211	0.87
27.8 - 29.8	149	1.23	0.40 - 0.44	194	0.86
29.8 - 32.8	150	1.15	0.44 - 0.48	167	0.80
32.8 - 37.6	151	1.00	0.48 - 0.51	136	1.00
37.6 - 42.3	155	0.69	0.51 - 0.53	114	1.02
42.3 - 48.9	154	0.81	0.53 - 0.56	81	0.97
48.9 - 62.9	156	0.89	0.56 - 0.58	54	1.04
62.9 - 139.9	155	1.06	0.58 - 0.60	33	1.53





Table 5. Continued.

h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $
1 9 -5	24	23	2 9 -2	41	48	3 9 3	24	22	4 9 8	27	24	6 9 1	43	42
1 9 -4	30	28	2 9 0	41	45	3 9 4	43	42	5 9 -11	28	24	6 9 2	32	32
1 9 -3	39	43	2 9 1	39	41	3 9 5	22	14*	5 9 -8	29	29	6 9 4	32	32
1 9 -1	37	46*	2 9 2	19	17	3 9 7	27	27	5 9 -6	23	24	7 9 -12	26	20*
1 9 0	30	39*	2 9 3	45	47	4 9 -12	27	20*	5 9 -5	35	36	7 9 -11	25	18*
1 9 2	47	48	2 9 4	22	20	4 9 -11	25	21	5 9 -3	34	39	7 9 -9	32	32
1 9 3	32	30	2 9 5	24	23	4 9 -9	32	34	5 9 -2	39	40	7 9 -7	22	21
1 9 4	20	20	2 9 6	40	37	4 9 -8	23	22	5 9 0	40	40	7 9 -6	33	35
1 9 5	41	38	2 9 8	27	21*	4 9 -7	23	19	5 9 1	29	29	7 9 -4	32	33
1 9 6	21	17	3 9 -10	27	25	4 9 -6	41	42	5 9 2	20	21	9 9 -3	27	29
1 9 7	29	25	3 9 -9	25	24	4 9 -5	16	14	5 9 3	40	38	7 9 -1	31	34
1 9 8	34	32	3 9 -7	35	36	4 9 -4	35	35	5 9 6	30	26	7 9 0	23	25
2 9 -11	29	23*	3 9 -6	21	18	4 9 -3	33	34	6 9 -12	26	20*	7 9 2	30	28
2 9 -10	25	21	3 9 -5	26	27	4 9 -1	40	42	6 9 -10	26	24	7 9 5	29	24
2 9 -8	36	35	3 9 -4	39	44	4 9 0	32	35	6 9 -9	22	18	6 9 -11	28	23
2 9 -7	28	24	3 9 -2	32	36	4 9 2	34	36	6 9 -7	28	34	8 9 -8	24	26
2 9 -6	18	18	3 9 -1	34	39	4 9 3	26	25	6 9 -5	30	28	8 9 -6	30	29
2 9 -5	41	41	3 9 0	19	21	4 9 4	23	21	6 9 -4	41	41	8 9 -5	29	32
2 9 -4	20	16	3 9 1	48	50	4 9 5	27	29	6 9 -2	37	38	8 9 -3	32	34
2 9 -3	31	33	3 9 2	28	27	4 9 7	26	23	6 9 -1	28	33	8 9 -2	25	28

in the anisotropic refinement. The value of  $R$  was obtained by using all the observed reflexions in the refinement, while the value of  $wR$  was obtained by using only the 1480 reflexions where  $0.80 < |F_o|/|F_c| < 1.25$ . Reflexions with  $|F_o|/|F_c|$ -ratios outside these limits are denoted with an asterisk in Table 5.

The shifts in all parameters were less than 5 % of their estimated standard deviations in the last cycle of refinement. The weighting scheme used was satisfactory as indicated by the near constancy of the averages of  $w(|F_o| - |F_c|)^2$  between different  $|F_o|$  and  $\sin \theta$  intervals (*cf.* Table 4).

A final difference synthesis calculated by using the refined parameters showed the presence of a peak of the magnitude  $3 e/\text{\AA}^3$  at the europium position. The other parts of the electron density maps showed only small spurious peaks  $0.5 - 1 e/\text{\AA}^3$ , above a slightly varying background.

The atomic parameters with their corresponding standard deviations are given in Table 3 while the observed and calculated structure factors are compared in Table 5.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances and angles of interest for the following discussion are given in Table 6. Symmetry related atoms have been given superscripts of the following significance.

i	$-x, -\frac{1}{2} + y, -z;$	vi	$1 - x, -\frac{1}{2} + y, -z;$
ii	$1 - x, \frac{1}{2} + y, 1 - z;$	vii	$1 + x, y, 1 + z;$
iii	$x, y, 1 + z;$	viii	$x, 1 + y, z;$
iv	$-x, -\frac{1}{2} + y, 1 - z;$	ix	$1 - x, \frac{1}{2} + y, -z;$
v	$1 + x, y, z;$	x	$-x, \frac{1}{2} + y, -z;$

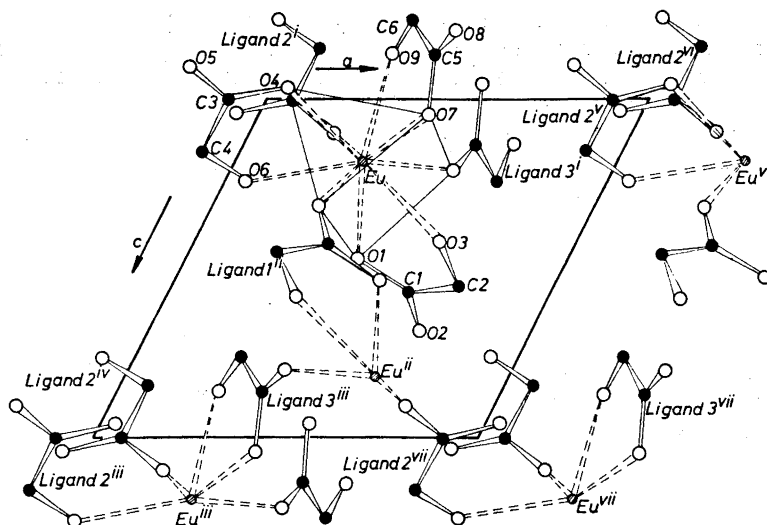
where  $x, y,$  and  $z$  are coordinates of the crystal-chemical unit given in Table 3.

The structure is a three-dimensional network, whose features are illustrated in projections perpendicular to  $b$  and  $c$ , shown in Figs. 1 and 2, respectively. The network is built up of ligand chains along  $b$  formed by applying the symmetry operation  $2_1$  on the three ligands. The glycolate ions within each chain are linked by hydrogen bonding (see p. 3358) and the various chains are cross-linked by coordination of the oxygen atoms to europium.

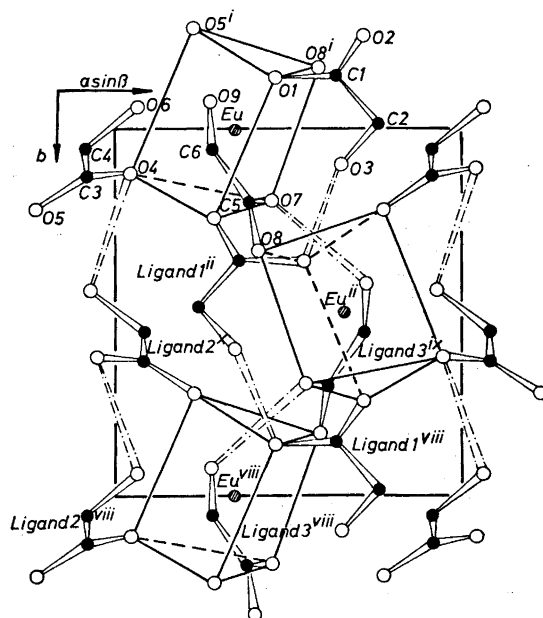
Table 6. Selected bond distances (in Å) and angles with their corresponding standard deviations.

Within the coordination polyhedron			
Eu—O(1)	2.44(2)	O(1)—O(2 <sup>II</sup> )	3.40(3)
Eu—O(2 <sup>II</sup> )	2.40(2)	O(5 <sup>I</sup> )—O(4)	3.53(3)
Eu—O(3)	2.62(2)	O(8 <sup>I</sup> )—O(7)	3.23(3)
Eu—O(4)	2.53(2)	O(3)—O(2 <sup>II</sup> )	3.07(2)
Eu—O(5 <sup>I</sup> )	2.45(2)	O(3)—O(7)	2.91(2)
Eu—O(6)	2.70(2)	O(3)—O(8 <sup>I</sup> )	2.72(3)
Eu—O(7)	2.41(2)	O(6)—O(1)	3.08(3)
Eu—O(8 <sup>I</sup> )	2.47(2)	O(6)—O(2 <sup>II</sup> )	2.99(3)
Eu—O(9)	2.55(2)	O(6)—O(5 <sup>I</sup> )	2.87(3)
O(2 <sup>II</sup> )—O(7)	3.22(2)	O(9)—O(4)	2.93(3)
O(2 <sup>II</sup> )—O(4)	2.88(2)	O(9)—O(5 <sup>I</sup> )	2.74(3)
O(4)—O(7)	3.26(2)	O(9)—O(8 <sup>I</sup> )	2.97(3)
O(1)—O(5 <sup>I</sup> )	3.09(3)	∠O(1)—Eu—O(3)	65.6(6)
O(1)—O(8 <sup>I</sup> )	2.89(3)	∠O(4)—Eu—O(6)	62.7(6)
O(5 <sup>I</sup> )—O(8 <sup>I</sup> )	2.95(3)	∠O(7)—Eu—O(9)	65.5(6)
Within ligand 1 $O(3)-C(2)-C(1) < O(1)$ $O(2)$			
C(1)—O(1)	1.36(3)	∠O(1)—C(1)—O(2)	122(2)
C(1)—O(2)	1.27(3)	∠O(1)—C(1)—C(2)	122(2)
C(1)—C(2)	1.58(5)	∠O(2)—C(1)—C(2)	116(2)
C(2)—O(3)	1.41(4)	∠O(3)—C(2)—C(1)	108(3)
O(1)—O(3)	2.66(3)		
Within ligand 2 $O(6)-C(4)-C(3) < O(4)$ $O(5)$			
C(3)—O(4)	1.32(3)	∠O(4)—C(3)—O(5)	124(2)
C(3)—O(5)	1.31(3)	∠O(4)—C(3)—C(4)	123(2)
C(3)—C(4)	1.48(4)	∠O(5)—C(3)—C(4)	113(2)
C(4)—O(6)	1.46(4)	∠O(6)—C(4)—C(3)	111(2)
O(4)—O(6)	2.72(3)		
Within ligand 3 $O(9)-C(6)-C(5) < O(7)$ $O(8)$			
C(5)—O(7)	1.31(3)	∠O(7)—C(5)—O(8)	120(2)
C(5)—O(8)	1.29(3)	∠O(7)—C(5)—C(6)	120(2)
C(5)—C(6)	1.51(4)	∠O(8)—C(5)—C(6)	120(2)
C(6)—O(9)	1.44(4)	∠O(9)—C(6)—C(5)	112(2)
O(7)—O(9)	2.69(3)		
Possible hydrogen bonds			
O(3)—O(1 <sup>II</sup> )	2.66(3)	∠C(2)—O(3)—O(1 <sup>II</sup> )	117(2)
O(6 <sup>x</sup> )—O(4)	3.00(3)	∠C(4 <sup>x</sup> )—O(6 <sup>x</sup> )—O(4)	107(2)
O(9 <sup>Ix</sup> )—O(7)	2.80(3)	∠C(6 <sup>Ix</sup> )—O(9 <sup>Ix</sup> )—O(7)	113(2)
		∠C(1 <sup>II</sup> )—O(1 <sup>II</sup> )—O(3)	104(2)
		∠C(3)—O(4)—O(6 <sup>x</sup> )	89(1)
		∠C(5)—O(7)—O(9 <sup>Ix</sup> )	98(1)



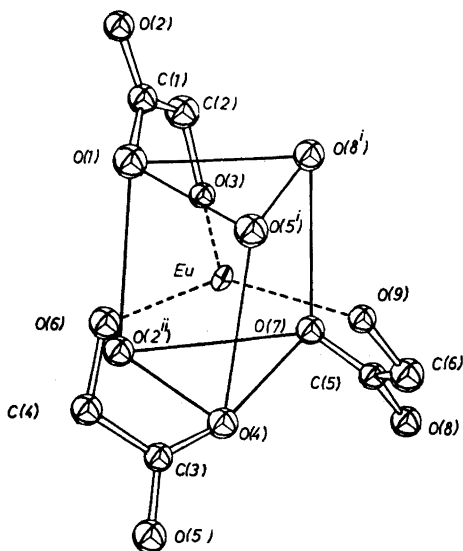


*Fig. 1.* Projection of the europium tris-glycolato structure perpendicular to *b*. The europium, carbon, and oxygen atoms are denoted by striped, black, and white circles, respectively. The symbols used for symmetry related atoms are explained on p. 3353. Bonds within the ligand are full-drawn, and the metal oxygen bonds are dashed.



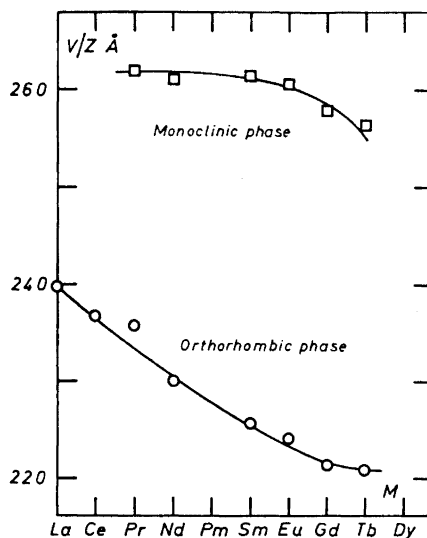
*Fig. 2.* Projection of the structure perpendicular to *c*. The symbols are the same as in Fig. 1. The most probable hydrogen bonds are denoted by the dashed and dotted lines.

The dimensions of the coordination polyhedra are approximately the same in the orthorhombic and the monoclinic rare earth trisglycolato phases. The way of stacking is, on the other hand, quite different, and results in the monoclinic compounds in the formation of large channels parallel to  $b$ . This is the cause of the large difference in volume per formula unit between the two phases, a difference which is equal to  $39 \text{ \AA}^3$  or approximately 15 % in the two europium compounds (*cf.* Fig. 4).



*Fig. 3.* A parallel projection of the coordination polyhedron in Euglyc drawn by using the program ORTEP. The atoms are represented by "thermal spheres" (or ellipsoide for the europium atom), formally scaled to include 50 % of the probability distribution. The root mean square displacements along the principal axes of the thermal ellipsoide are equal to 0.068 Å, 0.102 Å, and 0.148 Å, respectively.

*The coordination polyhedron.* The europium atom is nine-coordinated, and a parallel projection of the coordination polyhedron is shown in Fig. 3. It is of the tri-capped trigonal prism type previously described (*e.g.* Refs. 2 and 8). All ligands are bonded as chelates with the hydroxy oxygen in the equatorial, and one of the carboxylate oxygens at a corner position of the prism. Most metal-oxygen bond distances have values close to those found before in other nine-coordinated complexes of rare earths with an ionic radius close to that of europium (*e.g.* Refs. 2 and 8). The only exception is the distance Er-O(6) which is unusually long,  $2.70 \pm 0.02 \text{ \AA}$ .



*Fig. 4.* The unit cell volume per metal atom  $V/Z$  for the various monoclinic and orthorhombic rare earth tris-glycolate phases.

It is not surprising to find fairly large variations in the metal-oxygen bond distances in compounds of the type described here. Very special geometric conditions must obviously be present if equal coordination distances are to be observed in solid complexes where the ligand forms a chelate to one metal ion and a third bond to an adjacent one. These requirements are even more strengthened by the fact that the interatomic distances and bond-angles in the coordinated ligand cannot be distorted much from the corresponding "free ion" values. It is thus a good approximation to regard the ligand as a rigid body, with some rotational freedom around the single bonds (*vide infra* and Ref. 9).

A rigid body behaviour of the ligands offers a possible explanation for the long europium - oxygen bond distance (Eu - O(6)). A decrease of this distance with 0.1 Å can occur only if the bond angles in the chelate are decreased approximately 10°. So large distortions are improbable and have not been observed in other solid glycolato complexes.

The carbon - oxygen - metal angles within the chelates are all close to 120°, the mean value being  $118 \pm 1^\circ$ . The corresponding angle for the carboxylate oxygen which is not chelate bonded is larger,  $141 \pm 1^\circ$ . These findings are in agreement with the corresponding quantities in the orthorhombic Gdglyc phase.<sup>2</sup>

The coordination polyhedron in Euglyc is less distorted than that in Gdglyc. The two triangular faces of the prism are slightly tilted; the perpendicular distances from O(1), O(5<sup>i</sup>), and O(8<sup>i</sup>) to the plane formed by the opposite oxygens are 3.40 Å, 3.51 Å, and 3.23 Å, respectively.

The average distances between the coordinated oxygen atoms are approximately the same in the two tris-glycolato phases, *viz.* 3.04 Å for Euglyc and 3.01 Å for Gdglyc. The averages for the six shortest oxygen - oxygen distances are 2.84 Å and 2.80 Å, respectively. These facts indicate that the repulsive forces between the coordinated oxygen atoms ought to be of the same magnitude in the two types of polyhedra.

The europium atom is situated 0.07 Å from the plane formed by the three equatorial hydroxy - oxygens. The corresponding distances from the planes formed by ligands 1, 2, and 3 are larger, 0.94 Å, 0.44 Å, and 0.64 Å, respectively. Similar features have also been observed in the Gdglyc structure.

*The ligands.* Corresponding inter-atomic distances and angles within the three ligands are not significantly different from one another, or from the values found in non-chelated glycolato complexes.<sup>10,11</sup> It thus seems to be a good approximation to consider the ligand as a rigid body, as far as bond distances and bond angles are concerned. Two of the ligands are approximately planar (*cf.* Table 7), while the third deviates significantly from planarity, the hydroxy - oxygen being twisted 0.22 Å ( $\sim 9^\circ$ ) out of the plane formed by the C - COO group. Possible structural reasons for this twist might be the following. The distance Eu - O(6) changes less than 0.01 Å if O(6) is rotated so that the ligand is planar. The distance O(6) - O(5<sup>i</sup>) is then shortened from 2.87 Å to 2.54 Å with an increasing oxygen - oxygen repulsion as a result. The hydrogen bond donor angle C(4) - O(6)  $\cdots$  O(4) is at the same time increased from 107° to approximately 134°. Especially the first factor is expected to make the planar form of the ligand energetically less favoured than the twisted one.

Table 7. The deviation in Å of the europium and ligand atoms formed by the equatorial hydroxy oxygens and the C-COO groups, respectively.

Atom	Distance in Å	Atom	Distance in Å	Atom	Distance in Å	Atom	Distance in Å
Eu	-0.07	Eu	-0.94	Eu	0.44	Eu	-0.64
O(3)	0.00	O(1)	0.00	O(4)	-0.00	O(7)	0.00
O(6)	0.00	O(2)	0.00	O(5)	-0.01	O(8)	0.00
O(9)	0.00	C(1)	-0.01	C(3)	0.01	C(5)	0.01
		C(2)	0.00	C(4)	0.00	C(6)	0.00
		O(3)	0.02	O(6)	-0.22	O(9)	0.05

*Possible hydrogen bonds.* Several oxygen-oxygen distances are compatible with hydrogen bonding (Table 6) and the most probable bond scheme is outlined in Fig. 2. This choice, where the hydroxy hydrogen in each ligand is bonded to the chelate forming carboxylate oxygen in a symmetry related ligand, is based upon the following considerations:

*a.* Hydrogen bonding between two oxygen atoms in the same coordination polyhedron is improbable as it leads to europium-hydrogen distances less than 2.4 Å. This quantity can, for instance, be compared with the average distance,  $3.12 \pm 0.05$  Å, between samarium and the hydrogen atoms of coordinated water molecules in  $\text{Sm}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ .<sup>12</sup> The bond scheme outlined in Fig. 2 has all estimated metal-hydrogen distances larger than 3.0 Å, a reasonable minimum distance in compounds of this type.

*b.* The angles  $\text{CO}(\text{H}) \cdots \text{O}$  might be expected to lie in the interval  $110^\circ - 120^\circ$ .<sup>13</sup> This is very nearly the case for the bond scheme outlined in Fig. 2; the average angle is equal to  $112 \pm 3^\circ$ .

The chelate bonded carboxylate oxygens act as hydrogen bond acceptors with an average  $\text{O}(\text{H}) \cdots \text{OC}$  angle of  $97^\circ$ . This quantity is smaller than the value found in  $\text{Gdglyc}$  ( $110^\circ$ ) and in tris (hydroxyacetato) erbium(III) dihydrate ( $121^\circ$ ).

*Remarks on the variation of the lattice parameters.* The unit cell dimensions of the monoclinic Pr-Tb phases are shown in Fig. 4. The corresponding data for the orthorhombic phases are also included for comparison. The unit cell volume is approximately constant both for the monoclinic Pr-Eu phases and for the orthorhombic Gd-Tb phases. The near constancy in the unit cell volume for the rare earths with the smallest ionic radius indicates that the sizes of the coordination polyhedra are approximately the same. This may be due to increasing oxygen-oxygen repulsions as discussed by Albertsson<sup>14</sup> and Grenthe.<sup>9</sup>

The near constancy in unit cell volume for the monoclinic Pr-Eu phases also indicates an approximate constancy in the size of the coordination polyhedra. However, this constancy cannot be explained as a result of increasing oxygen-oxygen repulsions; a more probable explanation may be that the network of hydrogen bonds prevents a change in size of the coordination polyhedra. Detailed information in these matters cannot be obtained until structure data (including the positions of the hydrogen atoms) are available for at least two monoclinic compounds.

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